

# The effect of pulse width on the microstructure of d.c.-plasma-nitrided layers

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## Abstract

Modern ion nitriding equipment are powered by pulsed sources in order to prevent arcing and overheating. In industrial applications, the pulse frequency is usually adjusted to set the working temperature. However, frequency variations may drastically affect the plasma species population, and consequently, the microstructure of the final nitrided layer. In this study, AISI-409 steel was nitrided in a mixture of 20% N<sub>2</sub>–80% H<sub>2</sub> using a d.c. power source. The depth and microstructure of the nitrided layer were assessed as a function of the time that the voltage was off,  $t_{\text{off}}$ , in the range of 1–4 ms during a 10 ms pulse cycle. The results suggested that both the microstructure and mechanical behavior of the nitrided layer were affected by  $t_{\text{off}}$ . Long  $t_{\text{off}}$  values imply a deleterious effect on the mechanical properties of the nitrided layers. © 1999 Elsevier Science S.A. All rights reserved.

**Keywords:** Ion bombardment; Plasma nitriding; Pulsed plasma

## 1. Introduction

Among various physical, chemical, and metallurgical methods currently employed to harden steel surfaces, ion nitriding has gained considerable importance in the past few years. The experimental apparatus consists of a hermetically closed vessel containing two electrodes: an anode, and a cathode, where the metallic workpiece is placed. A nitriding atmosphere, typically consisting of a mixture of N<sub>2</sub> and H<sub>2</sub>, is established at pressures that may vary from 100 to 1500 Pa. The voltage applied between the electrodes usually lies in the range of 0–800 V. Ionic species generated in the plasma atmosphere are accelerated by the applied potential towards the surface of the specimen. As a result of the plasma/surface interaction, a hard layer is formed. This layer is normally composed of two zones, i.e. a compound zone near the surface where Fe<sub>2–3</sub>N- $\epsilon$  and/or Fe<sub>4</sub>N- $\gamma'$  can be formed, and a deeper diffusion zone, consisting of a solid solution of N in Fe and precipitates of nitrided alloying elements dispersed on the microstructure [1].

Plasma nitriding brings many advantages as compared to the salt bath technique, such as the absence of

toxic byproducts, relatively short treatment times, and the inherent versatility to tailor the microstructure and, therefore, the properties of the resulting nitrided layer. However, a few limitations can still be encountered, such as the formation of undesirable cathodic arcs, when intricate geometries or surfaces with protuberances or oxide phases are plasma-treated. Arcing can be overcome by replacing a d.c. power supply with a pulsed power supply. Nowadays, pulsed plasma equipment is readily available, which can operate at frequencies from 1 to 10 kHz. The use of pulsed sources enables the temperature of the specimen to be controlled by simply adjusting the width of the pulse,  $t_{\text{on}}$ , without changing the bias voltage. Even though plasma reactors equipped with a pulsed power supply have been available for over a decade, only recently have extensive studies been published regarding the effect of the pulse aspect on the final properties of the nitrided layers [2,3].

It could be suggested that plasma species, such as ions and energetic neutrals, have a great effect on the kinetics of the nitriding process, since plasma-nitriding times are generally shorter than with gas nitriding. However, controversy still remains as to which plasma species are responsible for the nitriding process [3–5]. Several theoretical models have been proposed to explain the kinetics of the process. For instance, Tibbetts [5]

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investigated the nitriding behavior of samples biased to repel positive ions and obtained similar rates to those of unbiased samples, leading to the conclusion that only energetic and neutral species were responsible for the formation of a nitrided layer. Another group of models takes into account the effect of the mass transfer from ionized atoms and molecules. Hudis et al. [6] suggested that the mass transfer from  $N_2^+$  and  $NH_2^+$  species is the predominant but not unique mechanism in ion nitriding, although the ionized atmosphere itself does not consist in a sufficient condition. These species are actually required to strike the surface of the workpiece. Recently, Gantois et al. [7] nitrided steels in the post-discharge region, which contains only electrically neutral species. The authors obtained results similar to those of plasma-nitrided samples. Thus, they were able to demonstrate that species with long life spans, such as excited neutral species and atomic nitrogen, were responsible for post-discharge nitriding. In recent years, a great effort has been devoted to rationalize the plasma diagnosis during ion nitriding [8–12]. The issuing results have established the importance of the excited neutral species in the ion-nitriding process, as well as that of the population modifications during the plasma afterglow. As the plasma is extinct (afterglow), all emission lines of the species decrease approximately exponentially with time. A few of them, especially those of the excited species  $N_2(A^3\Sigma_u^+)$ , can be observed for several milliseconds after the plasma itself has been extinct [13]. Others decay in much shorter times, as is the case of the  $N_2^+$  species, from which only 10% of the initial population still remains after 100  $\mu$ s [14]. This effect is particularly important for the study of pulsed plasma nitriding as during the time between pulses ( $t_{off}$ ), significant modifications can take place in the composition of the plasma causing variations in the nitriding kinetics, thus affecting the characteristics of the nitrided layer. The  $NH^+$  radical is one of the species with a short life span. These species are produced only by electronic collisions, and they are extinguished as soon as the plasma current ceases. The concentration of these species depends on the content of hydrogen in the atmosphere. In fact, the relative population of all plasma species depends on the hydrogen content in the mixture [13,15]. For a mixture containing 10%  $H_2$ , an increase in the population of species such as  $NH^+$ ,  $Fe$ ,  $N^+$ ,  $N_2^+$ ,  $N_2^*$ , and  $N$  has been observed, with  $Fe$  and  $NH^+$  being the most affected species. In addition, at that  $H_2$  level, relatively hard surfaces have been easily obtained [13].

Therefore, in the light of arguments such as the accentuated exponential decay of  $NH^+$  as compared to  $N_2$ , and the effect of hydrogen in the plasma atmosphere changing the hardness of the nitrided layer, as well as the distribution of active species, it can be anticipated that pulsed plasma parameters can affect the nitriding mechanism. Thus, the purpose of this work is to contribute towards understanding the effect of one of these parameters, i.e. the pulse width,  $t_{on}$ , on the final properties of the nitrided layer. To that end, AISI-409 steel was investigated, as the main characteristic of this steel is its low carbon and high chromium content, which are prone to the formation of a diffusion zone, but prevent the precipitation of carbonitrides in the nitrided layer. This steel was also chosen because of the importance in increasing the technological use of plasma-hardened ferrite stainless steel for industrial applications.

## 2. Experimental

AISI 409 steel samples with 10 mm  $\times$  10 mm cross-sections were ground and polished to a 1  $\mu$ m finish in alumina slurry and subsequently rinsed in acetone prior to nitriding. The nominal chemical composition of the steel samples employed herein can be found in Table 1.

Nitriding experiments were carried out in a pulsed plasma apparatus, consisting mainly of a reaction chamber, a vacuum system, a power supply, and a data acquisition system (Fig. 1). In addition to a pair of electrodes and a sample holder, the plasma chamber also included a borosilicate tube, 400 mm in length and 320 mm in diameter, yielding a total volume of 0.32 m<sup>3</sup>. The ends of the tube were sealed by two stainless-steel flanges. The bottom flange held the gas inlets, vacuum connection, pressure sensors, and thermocouples. The continuously adjustable power supply maintained a maximum output of 800 V d.c. and a current of 2 A. In addition to the d.c. source, a square pulsed voltage could also be obtained by varying the width of a pulse from 1 to 9 ms, in a 10 ms cycle.

The samples were nitrided in an atmosphere of 20%  $N_2$ –80%  $H_2$  kept at a pressure of 600 Pa. The plasma chamber was initially evacuated and purged with the working gas at a pressure of 200 Pa. Next, as the samples were heated up to 500°C, assisted by a glow discharge, the pressure of the chamber was simultaneously increased to 600 Pa. After a soaking period of 3 h at 500°C, the power was shut off. A set of experiments,

Table 1  
Nominal composition of AISI-409 steel (in wt.%)

Element	C	Mn	Si	Cr	Ni	Mo	Al	V	Nb	Ti
Concentration (wt.%)	0.07	0.14	0.36	11.23	0.33	0.013	0.025	0.048	0.11	0.13

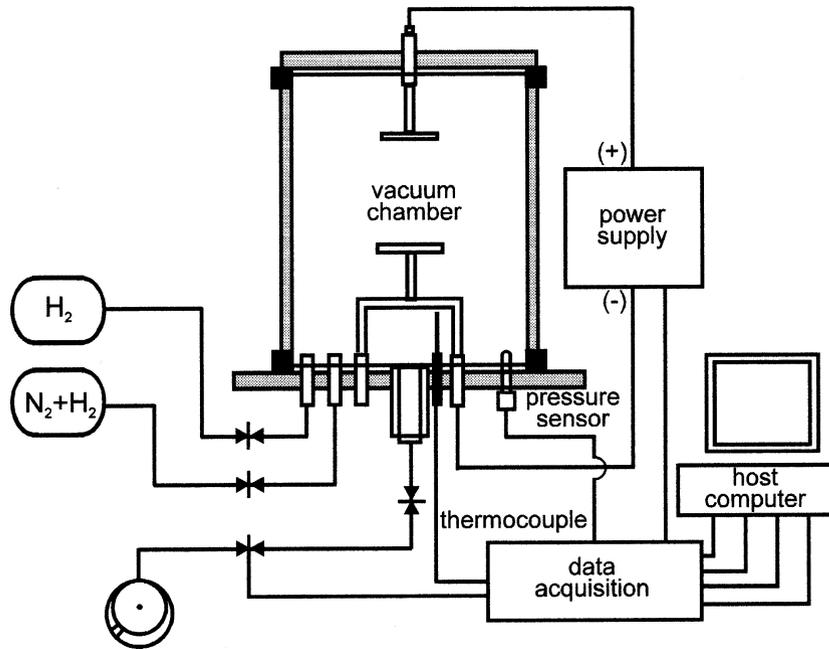


Fig. 1. Schematic representation of pulsed plasma equipment.

with varying  $t_{\text{off}}$  values, was carried out. As the parameter  $t_{\text{off}}$  was set to a new value, both the voltage and current had to be adjusted in order to maintain the sample at a constant temperature of 500°C. Table 2 summarizes the range of  $t_{\text{off}}$  values investigated along with the corresponding voltage and current values.

The AISI 409 nitrided steel samples were then examined to determine the thickness and microstructure of the compound layer. In addition, an analysis on the composition of superficial phases and nitrogen profile was also carried out. Finally, the microhardness profile of the samples was also measured. The nitrogen concentration profile was obtained by energy-dispersive spectroscopy, using a solid state Si–Li detector with resolution of 140 eV, and equipped with a Be window. In order to observe the evolution of the microstructure towards the bulk of the samples, the nitrided surfaces were progressively worn using a 1  $\mu\text{m}$  alumina slurry. After each polishing step, the surfaces were analyzed by X-ray diffraction (XRD).

Table 2  
Values of  $t_{\text{off}}$  investigated with corresponding voltages and current

Sample label	$t_{\text{off}}$ (ms)	Voltage (V)	Current (mA)
A0	0	500	493
A1	1	515	500
A2	2	527	485
A3	3	523	480
A4	4	513	499
A5	5	514	492

### 3. Results and discussion

#### 3.1. Effect of $t_{\text{off}}$ on the nitrided surface

Fig. 2 shows the microstructure of an AISI 409 nitrided layer obtained with  $t_{\text{off}}$  set to 1 ms. Other than slight differences that can be attributed to etching effects, the overall aspect of the nitride layer is typical of all samples, regardless of  $t_{\text{off}}$ . Such a nitrided layer revealed the presence of both transformed (dark areas) and non-transformed regions (bright areas). The microhardness of those regions was measured resulting in values up to 800 HV for the former and around 1000 HV for the latter. Additional work on nitrided Fe–Cr alloys can be found elsewhere [16]. Results from X-ray and electron diffraction suggest that the transformation process relies simply on the conversion of a very fine dispersion of homogeneously precipitated CrN characterized by a state of high interfacial energy, to an aggregate of large CrN needles in a ferritic matrix.

The X-ray patterns obtained herein indicated the presence of both  $\gamma\text{-Fe}_4\text{N}$  and  $\epsilon\text{-Fe}_{2-3}\text{N}$  phases on the nitrided surfaces. This result seems to contradict the results of Mortimer et al. [16]. A careful inspection of Fig. 3 (samples A0 and A4) reveals that the relative intensity of peaks corresponding to those two phases is higher than that of the  $\alpha\text{-Fe}$  phase. Since Fig. 2 does not show any substrate/compound zone interface, and therefore, this result clearly implies the superficial coexistence of nitrides and  $\alpha\text{-Fe}$ .

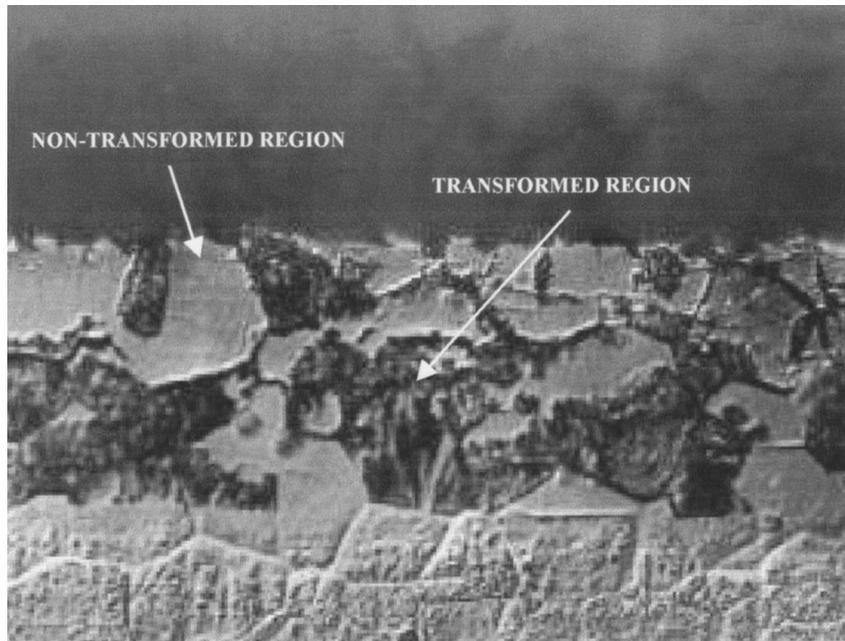


Fig. 2. Microstructure of nitrided layer for  $t_{\text{off}}=1$  ms.

The XRD pattern corresponding to sample A4 ( $t_{\text{off}}=4$  ms) is in contrast with the others, in terms of both the relative intensities and the width of the peaks. In order to establish a qualitative wear resistance comparison, samples were progressively polished, and the abraded surfaces were analyzed by XRD. Fig. 4 shows the diffraction patterns obtained from samples nitrided at two reasonably distinct  $t_{\text{off}}$  values (1 ms and 4 ms).

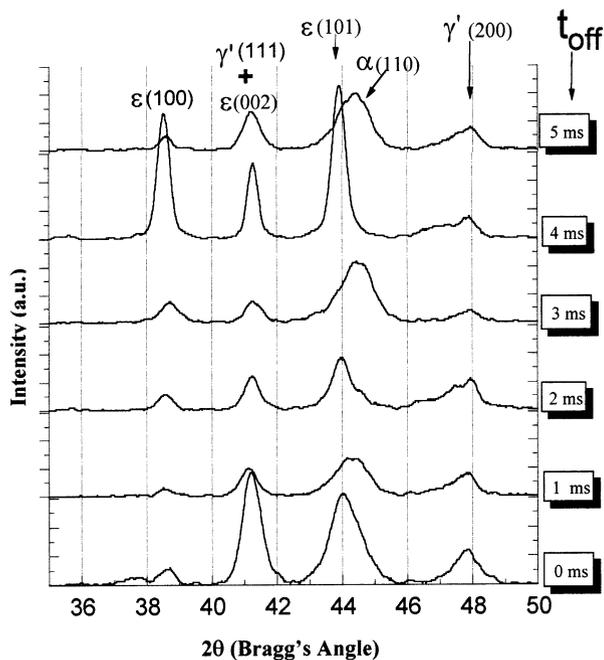


Fig. 3. XRD pattern of nitrided surfaces for different values of  $t_{\text{off}}$ .

Whereas it took 1000 s to remove the  $\gamma'$ -phase of the sample nitrided with  $t_{\text{off}}=1$  ms, diffraction peaks of the sample nitrided at  $t_{\text{off}}=4$  ms vanished following abrasion for only 10 s. This can be attributed either to the presence of a thinner compound zone, or to poor substrate-layer adherence and/or particle adhesion. The first hypothesis can be ruled out as the intensities of the nitride peaks present in the compound zone of sample A4 were generally higher than those of the remaining samples, suggesting that the corresponding compound zone is not thinner than the others. The second hypothesis appears to be consistent, as residual stresses usually develop from lattice mismatches typical of the coexistence of  $\epsilon$ - $\text{Fe}_{2-3}\text{N}$  and  $\gamma'$ - $\text{Fe}_4\text{N}$  or between substrate and compound zone. Either way, the results clearly indicated that a high  $t_{\text{off}}$  value was deleterious to the mechanical properties of the surface, as the nitride phases of such samples could be easily removed.

### 3.2. Effect of $t_{\text{off}}$ on the diffusion zone

The diffusion zone consists of nitrogen forming a solid solution with the Fe matrix and precipitates of nitrides from alloying elements. Particularly for AISI-409 steel, the nitride-forming alloying elements are essentially Cr, Ti, and Nb. According to Fick's second law, the penetration depth of nitrogen depends on the diffusion coefficient of the matrix and on the concentration gradient of atomic nitrogen. The diffusion coefficient can be modified by the population of defects which, in turn, is related to the rate of ionic sputtering

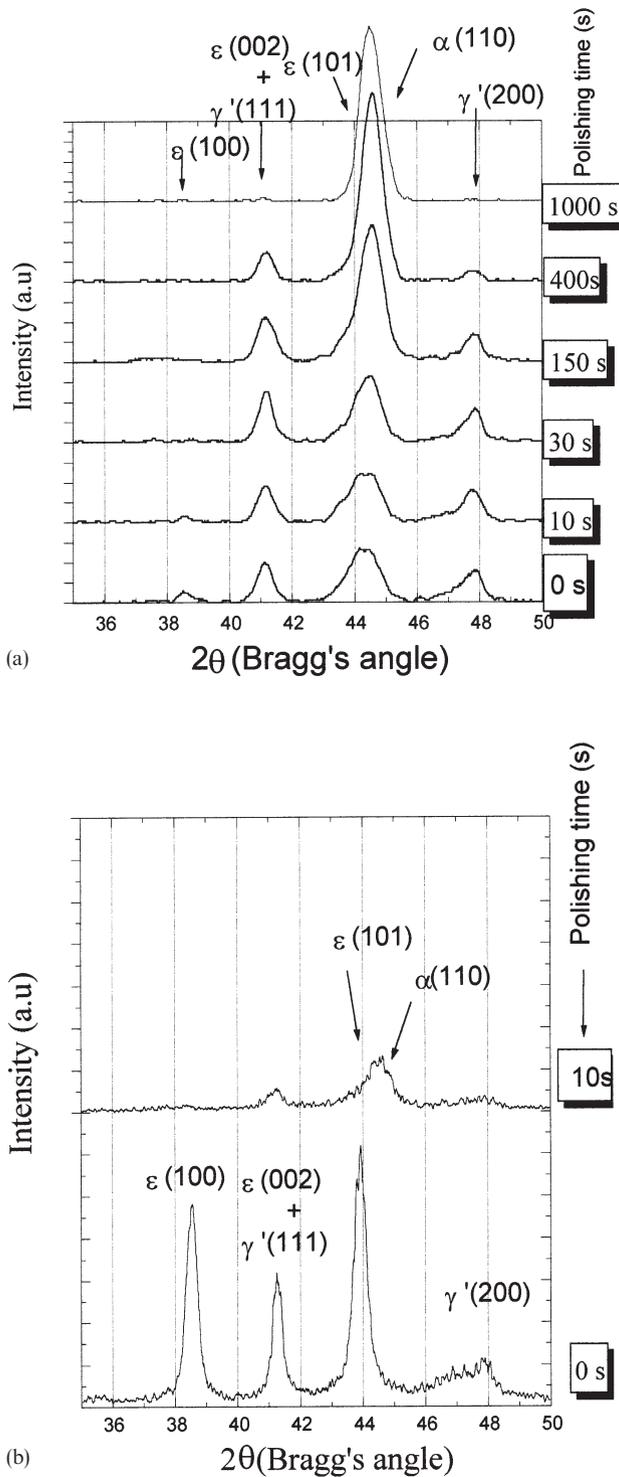


Fig. 4. XRD pattern obtained after progressive wear for samples nitrided with (a)  $t_{\text{off}}=1$  ms and (b)  $t_{\text{off}}=4$  ms.

at the surface. The concentration gradient can be modified by varying the concentration of atomic nitrogen at the surface of the specimen. In this case, nitrogen is produced either by the dissociation of  $N_2$  molecules or by the transformation of the primary nitrides into secondary nitrides. As  $t_{\text{off}}$  increases, the time-averaged

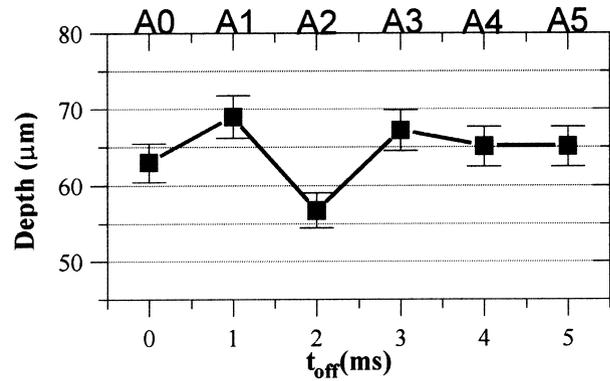


Fig. 5. Penetration depth of the diffusion zone as a function of  $t_{\text{off}}$ .

sputtering rate decreases, thus reducing the number of defects and, consequently, the diffusion coefficient. The concentration of atomic nitrogen resulting from the transformation of primary nitrides into secondary nitrides also changes, as there is enough time for the sequence  $\text{FeN} \rightarrow \text{Fe}_{2-3}\text{N} \rightarrow \text{Fe}_4\text{N}$  to take place, with no interruption of the ionic sputtering process. Fig. 5 shows the penetration depth of the diffusion zone as a function of  $t_{\text{off}}$ . The thickness of the nitrided layer remained approximately constant for all samples, except A1 and A2. As the ionized species are present in the plasma atmosphere only within the initial stage of the afterglow (after 100 ms, only 10% of the population of species can still be observed), it can be concluded that the energetic neutrals are the most important species in the production of atomic nitrogen, since they have longer life span than the ionic species.

The nitrogen profiles confirm the XRD results in the sense that the concentration of nitrogen in the surface of sample A0, nitrided in steady state d.c., was the highest within the series, whereas that of sample A3, nitrided with  $t_{\text{off}}=3$  ms was the smallest. Likewise, the intensities of XRD peaks  $\gamma'$ -(111) and  $\epsilon$ -(002) were maximum for A0 and minimum for A3.

It has been reported that the population of ionized and excited species varies with  $t_{\text{off}}$  as the pulse is extinct, reaching its minimum at 2 ms and maximum at 3 ms [8]. This result may be used to explain the thinness of the nitrided layer as well as the unique nitrogen profile observed for sample A2 ( $t_{\text{off}}=2$  ms).

Further systematic studies on pulsed plasma are required to consolidate a better understanding of the ion nitriding process, as well as to establish optimum process parameters, mainly the average concentration of active species in the plasma. The use of a variable frequency power source with simultaneous plasma diagnostics is necessary to identify the species responsible for the formation of superficial phases and atomic nitrogen.

#### 4. Conclusions

1. The penetration depth of nitrogen is affected by  $t_{\text{off}}$ , especially at 0 and 2 ms, where the largest variations in the thickness of the nitrated layer have been observed.
2. The plasma ionized species are not the most important species involved in the nitriding process. Nitriding at  $t_{\text{off}}=5$  ms (a small population of ionized species) resulted in layers as thick as those produced at a d.c. discharge (large population of ionized species).
3. Nitriding at higher values of  $t_{\text{off}}$  was deleterious to the mechanical properties of the compound layer, approaching the inferior quality typical of gas-nitrated samples. The decrease in the abrasive wear resistance could be attributed to the formation of a two-phase compound zone ( $\gamma'+\epsilon$ ), which induced a substantial concentration of thermo-mechanical residual stresses.

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